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Changes in the concentration of iron in different size fractions during an iron enrichment experiment in the open Southern Ocean

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Abstract

An in situ iron enrichment experiment was carried out in the Southern Ocean Polar Frontal Zone and fertilized a patch of water within an eddy of the Antarctic Circumpolar Current (EisenEx, Nov. 2000). During the experiment, a physical speciation technique was used for iron analysis in order to understand the changes in iron distribution and size-fractionations, including soluble Fe (<200 kDa), colloidal Fe (200 kDa–0.2 μ m) and labile particle Fe (>0.2 μ m), throughout the development of the phytoplankton bloom.

Prior to the first infusion of iron, dissolved (<0.2 μ m) iron concentrations in the ambient surface seawater were extremely low (0.06 ± 0.015 nM) with colloidal iron being a minor fraction. For the iron addition, an acidified FeSO₄ solution was released three times over a 23-day period to the eddy. High levels of dissolved iron concentrations (2.0 ± 1.1 nM) were measured in the surface water until 4 days after the first iron infusion. After every iron infusion, when high iron concentrations were observed before storm events, there was a significant correlation between colloidal and dissolved iron concentrations ($[\text{Colloidal Fe}] = 0.7627[\text{Dissolved Fe}] + 0.0519$, $R^2 = 0.9346$). These results indicate that a roughly constant proportion of colloidal vs. dissolved iron was observed after iron infusion (~76%). Storm events caused a significant decrease in iron concentrations (<0.61 nM in dissolved iron) and changed the proportions of the three iron size-fractions (soluble, colloidal and labile particle). The changes in each iron size-fraction indicate that colloidal iron was eliminated from surface mixed layer more easily than particulate and soluble fractions. Therefore, particle and soluble iron efficiently remain in the mixed layer, probably due to the presence of suspended particles and naturally dissolved organic ligands. Our data suggest that iron removal through colloidal aggregation during phytoplankton bloom should be considered in the oceanic iron cycle.

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Keywords: Southern ocean; Iron enrichment experiment; Size-fractionated iron; Iron speciation

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1. Introduction

Several in-situ iron fertilization experiments have been performed to evaluate whether iron limitation controls phytoplankton production and biogeochemical processes in High Nutrient Low Chlorophyll (HNLC) waters, including the equatorial Pacific, the Australia sector of Southern Ocean and the subarctic Pacific (Martin et al., 1994; Coale et al., 1996, 2004; Boyd et al., 2000, 2004; Tsuda et al., 2003). This hypothesis also was investigated in the Atlantic sector of Southern Ocean by mesoscale iron infusions in an eddy of the Antarctic Circumpolar Current in 2000, during the EisenEx (Smetacek, 2001).

Although these previous in situ experiment and bottle incubation studies clearly showed that iron plays an important role in supporting phytoplankton biomass and nutrient consumption in HNLC regions (Martin and Fitzwater, 1988; de Baar et al., 1990, 1995; Martin et al., 1994; Takeda and Obata, 1995; Takeda, 1998; Coale et al., 1996, 2004; Boyd et al., 2000, 2004; Gervais et al., 2002; Tsuda et al., 2003), large uncertainties still remain in our understanding of the chemistry, biology and biogeochemical cycling of iron in the ocean (Hunter et al., 2001). For example, the source and chemical form of naturally supplied iron to the ocean surface is not well understood. Although previous laboratory studies have evaluated the biological availability of several iron species (Morel et al., 1991; Wells et al., 1991; Kuma and Matsunaga, 1995; Wells, 1999; Hutchins et al., 1999; Boye and van den Berg, 2000; Nishioka and Takeda, 2000; Timmermans et al., 2001; Nodwell and Price, 2001; Chen et al., 2003), we still have a poor understanding of the biological availability of different iron species to phytoplankton in seawater. As a consequence, there is a greater interest in determining iron speciation in seawater and iron dynamics in oceanic plankton ecosystem (Wells et al., 1995; de Baar and deJong, 2001). Cathodic stripping voltammetric studies have indicated the presence of strong Fe-complexing ligands (Gledhill and van den Berg, 1994; Rue and Bruland, 1995, 1997; Wu and Luther, 1995; van den Berg, 1995; Johnson et al., 1997; Witter and Luther, 1998), and recent studies have reported substantial amount of colloidal iron within the operationally defined dissolved phase (<0.2 or $<0.4 \mu\text{m}$) in natural seawater (Wells et al., 2000;

Nishioka et al., 2001b; Wu et al., 2001). There is, however, little information on the changes in concentrations of different iron forms within phytoplankton ecosystems, which is important for our understanding of the biogeochemical cycle of iron in the ocean. In-situ iron fertilization experiments are a useful approach for improving our understanding of iron chemistry, iron biology and biogeochemical cycling of iron in seawater (Gordon et al., 1998; Rue and Bruland, 1997; Bowie et al., 2001; Croot et al., 2001; Wells et al., 2003; Nishioka et al., 2003).

According to our previous studies (Nishioka and Takeda, 2000; Nishioka et al., 2001a, 2003), colloidal sized iron is the most dynamic fraction during phytoplankton growth. Thus, studies of iron dynamics in natural seawater should focus on iron complexation with organic ligands as well as the relationship between the abundance and distribution of physical fractionated iron and phytoplankton growth.

In the present study, details of changes in physical (size-fractionated) and chemical (Fe(II): Croot et al., 2004a,b; organic ligands: Boye et al., 2004) speciation of iron were investigated in the upper water column of the EisenEx iron fertilized patch in the course of the phytoplankton bloom development over 23 days. To conduct physical speciation, $0.2 \mu\text{m}$ pore-size and 200 kDa were used for size-fractionation of colloidal iron in seawater (Nishioka et al., 2001b). This report presents in detail the changes in the concentrations of iron in different size fractions during a phytoplankton bloom in the EisenEx study.

2. Materials and methods

2.1. EisenEx study

An in situ iron enrichment experiment was carried out in the Polar Frontal Zone of the Southern Ocean ($\sim 20^\circ\text{E}$, 48°S ; Fig. 1) in austral late spring (6–29 Nov. 2000) during cruise ANT XVIII/2 of *P.S. Polarstern*. A mesoscale eddy (diameter ~ 100 – 150 km) structure was selected to for the location of the iron-fertilized patch. An acidified $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution was added to mixed layer of an area of about 50 km^2 with the SF_6 tracer saturated seawater solution. The iron infusion was repeated three times with intervals of ~ 8 days during the 23-day experiment. The iron fertilized

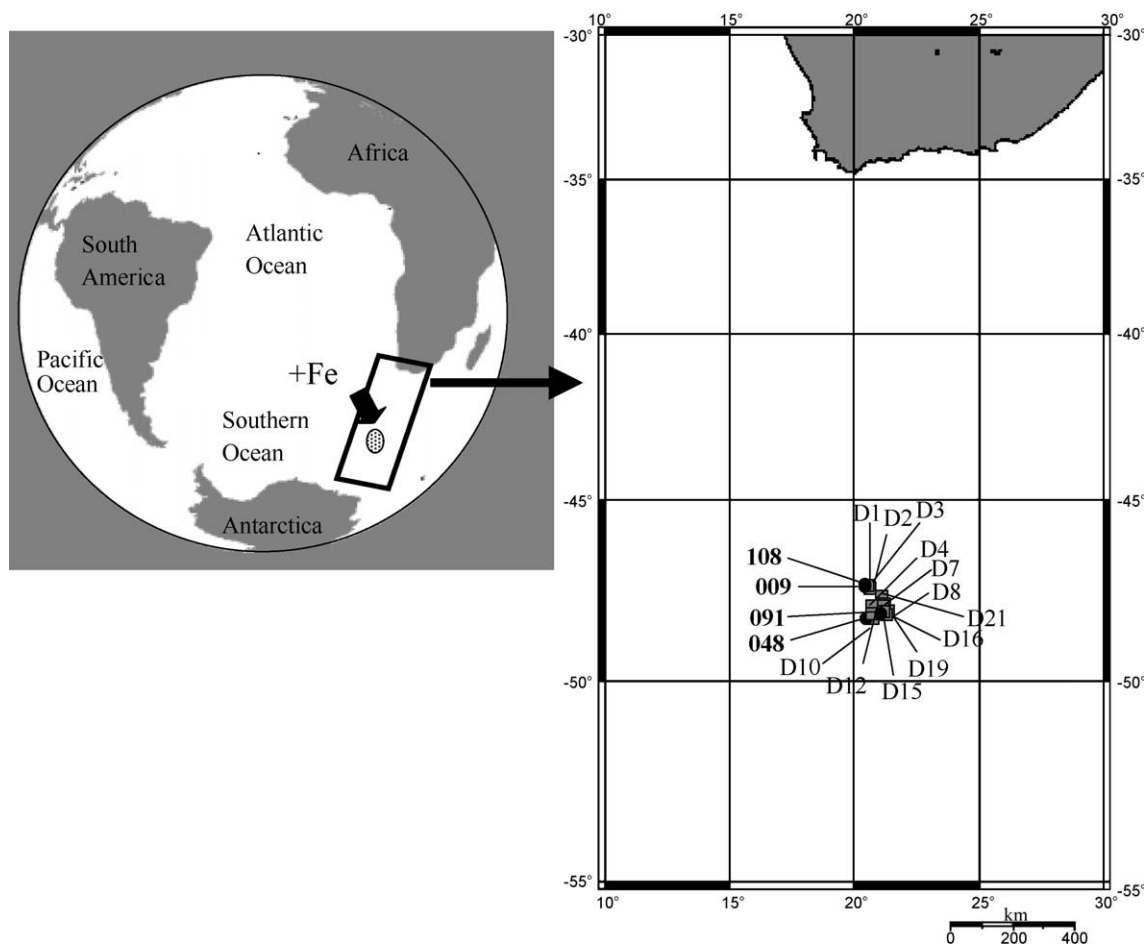


Fig. 1. Location of the EisenEx experiment.

patch was traced by surveys of the surface SF_6 concentration, and samplings were conducted at “In-patch stations”, where the highest SF_6 concentrations were observed, and “Out-patch stations”, within eddy waters that showed background SF_6 concentrations (Watson et al., 2001). During the experiment, the surface seawater temperature increased from 3.5 to 4.2 °C. The depth of the surface mixed layer increased from 40 to 80 m.

2.2. Sampling and analysis for size-fractionated iron

To characterize vertical profiles of iron in the patch, discrete samples were collected for iron analysis prior to the first iron infusion and during the experiment. Thirteen In-patch and four Out-patch

stations were sampled using acid-cleaned Teflon coated Go-Flo samplers (General Oceanics, Miami, FL, USA) suspended on Kevlar line. In general, samples typically were taken from 20, 40, 60, 80, 100 m depth at each In- and Out-stations (Croot et al., 2004a,b). At one of the out patch station (St. 091), a vertical profile from surface (50 m) to 1000 m depth was collected for size-fractionation study of iron and organic ligands in natural water (Boye et al., in preparation). Unfiltered and filtered ($<0.2 \mu\text{m}$; Sartorius Sartobran filter capsule 5231307H5) samples were collected into acid-cleaned 125 ml NALGENE Low density polyethylene (LDPE) bottles. Additional filtrate ($<0.2 \mu\text{m}$) samples collected in acid-cleaned 500 ml polycarbonate (PC) bottles were immediately size-fractionated by clean inline

ultrafiltration using a 200-kDa polyethylene hollow-fiber ultrafilter (Nishioka et al., 2001b) in a laminar flow clean air hood.

All unfiltered and filtrate (<200 kDa and <0.2 μm) samples were buffered at pH 3.2 with 10 M formic acid–2.4 M ammonium formate buffer solution. The concentration of Fe (III) in the buffered samples were determined using an automated Fe (III) flow injection analytical system (Kimoto Electric) employing chelating resin concentration and chemiluminescence detection (Obata et al., 1993, 1997). This method quantifies the chemically labile iron species which dissolve at pH 3.2 and react with the 8-hydroxyquinoline resin. The size-fractionation of iron was investigated. Measured total dissolvable iron concentrations were portioned into three size fractions: labile particulate iron (>0.2 μm ; Par-Fe; leachable iron at pH 3.2 from >0.2 μm particles), colloidal iron (200 kDa–0.2 μm ; Coll-Fe) and soluble iron (<200 kDa; Sol-Fe). We also defined Total dissolvable iron (TD-Fe) as detectable iron in unfiltered seawater and dissolved iron (Diss-Fe) as detectable iron in seawater which passed through 0.2 μm . The concentration of Par-Fe and Coll-Fe was calculated as the difference in measured Fe (III) concentrations of the TD-Fe and Diss-Fe, and Diss-Fe and Sol-Fe, respectively. (Nishioka et al., 2001b). The detection limit (three times the standard deviation) of Fe (III) concentrations for purified seawater (seawater passed through 8-hydroxyquinoline resin column three times) on this cruise was 0.015–0.032 nM. The relative coefficient of variation was within 5% ($n=12$) for replicate measurements of a seawater sample containing 0.53 nM Fe(III), within 6% ($n=9$) for 5.3 nM Fe(III).

3. Results

3.1. Biological response in the iron enriched patch

The biological responses to the iron addition during the EisenEx have been reported in Gervais et al. (2002). Four days after the 1st iron infusion, Chl. *a* concentration increase gradually in the iron enriched patch (from $\sim 0.5 \text{ mg/m}^3$) and reached the maximum value on day 21 ($\sim 2.5 \text{ mg/m}^3$), at the end of observations. The maximum integrated Chl. *a* concentration was four to five times higher than the

starting conditions of the experiment (Gervais et al., 2002).

3.2. Iron concentrations in the pre-iron release condition and out patch stations

Vertical profiles of iron concentrations in the different size fractions at different regions of the eddy prior to iron infusion (include out patch stations during the experiment) are shown in Fig. 2. Diss-Fe concentration (<0.2 μm) in surface mixed layer in this area was $0.06 \pm 0.02 \text{ nM}$ ($n=5$) and had nutrient-type distributions; characterized by depletion in the surface mixed layer and increased in deep waters (0.4 nM at 1000 m, Fig. 2 St. 091). On the other hand, average Par-Fe concentration in surface mixed layer were $0.11 \pm 0.09 \text{ nM}$ ($n=5$). With regard to physical speciation of dissolved iron, Sol-Fe and Coll-Fe concentrations in surface mixed layer were 0.04 ± 0.01 ($n=5$) and 0.02 ± 0.01 ($n=5$), respectively. Sol-Fe and Coll-Fe concentrations in deep water (300–1000 m) were 0.16 ± 0.03 ($n=9$) and 0.12 ± 0.07 ($n=9$), respectively (Fig. 2). In surface mixed layer, Sol-Fe, Coll-Fe and Par-Fe species comprised $25.4 \pm 8.5\%$, $14.5 \pm 7.4\%$ and $60.1 \pm 13\%$, respectively, of the TD-Fe concentration (Table 1). In contrast, the proportion in deep water was 44.3 ± 14.1 (Sol-Fe), 27.8 ± 10.0 (Coll-Fe) and 28.0 ± 10.3 (Par-Fe), respectively, of TD-Fe concentration (Table 1).

3.3. Iron concentrations in the patch during experiment

Vertical profiles of iron concentrations in the different size fractions at different times in the patch are shown in Fig. 3. The changes in mean value of iron concentrations in each size-fraction and chlorophyll *a* concentrations in the mixed layer over the time are shown in Fig. 4, while the percent contribution of each size fraction to the TD-Fe appear in Fig. 5. The mixed layer depth was $\sim 40 \text{ m}$ depth at the start of experiment, increasing to 60–80 m after the passage of several storm systems. The vertical distribution of iron at the in patch stations indicate that iron concentration was enhanced in the mixed layer by the iron infusion (Fig. 3A,B). At the first sampling point after the initial iron infusion (within 16 h from infusion), we observed a significant increases

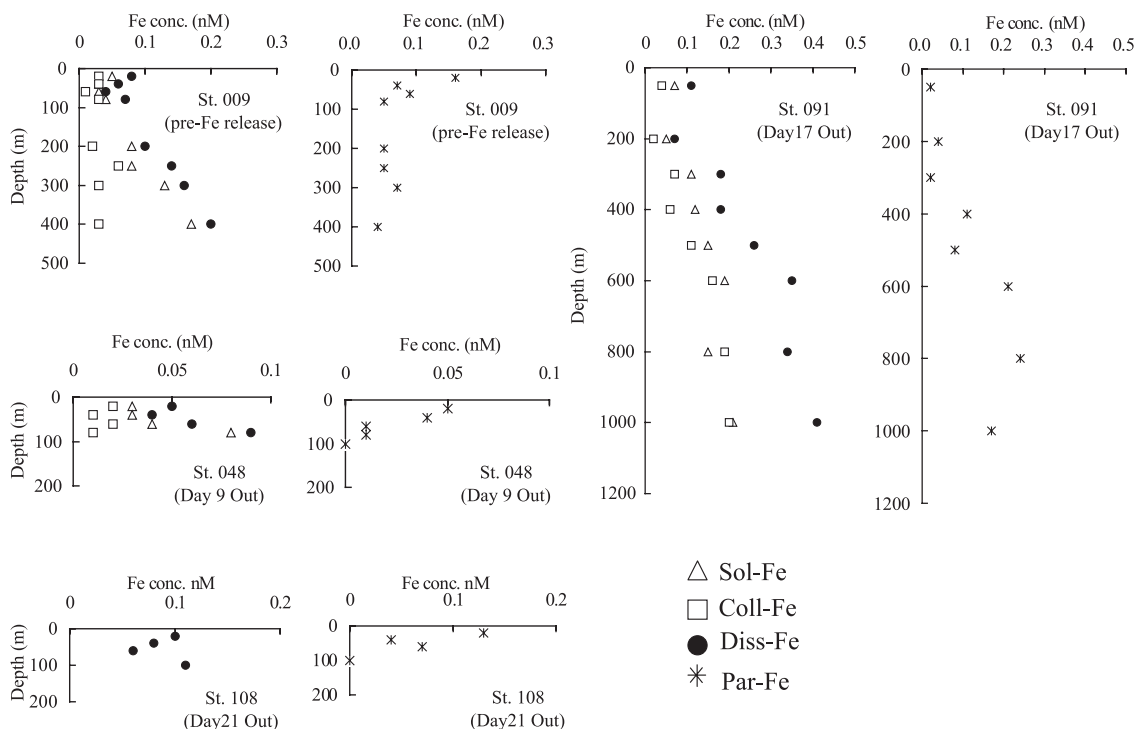


Fig. 2. Vertical profiles of iron concentration in different size fractions prior to iron infusion and at out patch stations, Soluble iron (Sol-Fe), Colloidal iron (Coll-Fe), Dissolved iron (Diss-Fe) and Labile particulate iron (Par-Fe). Day number indicates the time since first iron release.

of Diss-Fe (1.2 ± 0.64 nM) in the surface mixed layer with more than 80% of this iron being in a Coll-Fe form (200 kDa–0.2 μ m) (Fig. 3A). Elevated Diss-Fe concentrations (2.0 ± 1.1 nM) with a high proportion of Coll-Fe (>68%) remained in the mixed layer until 4 days after first iron infusion (Day 4). However, a strong storm event (between Days 4 and 7) caused Diss-Fe concentrations to decrease to <0.61 nM (Day 7) (Fig. 4). The second iron infusion also resulted

Diss-Fe concentrations being high (3.2 ± 1.4 nM) for 4 days until the second storm event. The third iron infusion was conducted on Day 16, just before the third storm event. Diss-Fe concentrations in surface mixed layer after this storm were low (0.18–0.4 nM) (on Days 19, 21; Figs. 3A and 4). High Par-Fe concentrations (1.3 ± 0.7 nM) were observed immediately following the 1st iron infusion and remained high until the second storm event (Fig. 4). After these

Table 1

Portion of soluble, colloidal and labile particulate Fe concentrations in total dissolvable Fe, and soluble and colloidal Fe concentrations in dissolved Fe at In and Out patch stations in surface mixed layer (ML) and natural deep water

	ML In patch station after iron release (high-iron periods) $n=24$	ML In patch station after storm event (post-storm periods) $n=21$	ML Out patch stations $n=5$	Deep layer (300–1000 m) Out patch stations $n=9$
Sol-Fe/TD-Fe (%)	14.2 ± 9.8	20.6 ± 8	25.4 ± 8.5	44.3 ± 14.1
Coll-Fe/TD-Fe (%)	50.0 ± 16.2	17.4 ± 9	14.5 ± 7.4	27.8 ± 10.0
Par-Fe/TD-Fe (%)	35.7 ± 13.4	62.0 ± 9	60.1 ± 13	28.0 ± 10.3
Sol-Fe/Diss-Fe (%)	22.9 ± 16	55.4 ± 20	65.2 ± 11.7	60.8 ± 14.5
Coll-Fe/Diss-Fe (%)	77.1 ± 16	44.6 ± 20	34.8 ± 11.7	39.2 ± 14.5

Sol-Fe: soluble Fe, Coll-Fe: colloidal Fe, Par-Fe: labile particulate Fe, TD-Fe: total dissolvable Fe, Diss-Fe: dissolved Fe.

storm events (before next iron infusion), Sol-Fe, Coll-Fe and Par-Fe species comprised $20.6 \pm 8\%$, $17.4 \pm 9\%$ and $62.0 \pm 9\%$, respectively, of the TD-Fe concentration (Table 1).

4. Discussion

4.1. Size-fractionated iron in natural condition in Southern Ocean

Pre-iron infusion analysis confirmed the extremely low ambient Diss-Fe concentrations in surface mixed layer around this experiment site in late austral spring. Before iron infusion, the potential photochemical efficiency of photosystem II (Fv/Fm) in phytoplankton was low (~ 0.30 by FRRF) (Gervais et al., 2002). After the iron infusion, a clear biological response was observed in iron-enriched waters (Gervais et al.,

2002). These results indicate that iron limits phytoplankton growth at this site in late austral spring, and the observed iron, 0.06 ± 0.02 nM ($n=5$) in Diss-Fe and 0.11 ± 0.09 nM ($n=5$) in Par-Fe, in the surface mixed layer before iron infusion was at limiting concentrations.

In our size-fractionated method, Coll-Fe concentration was calculated by differences of Diss-Fe and Sol-Fe concentration. Wells (2003) pointed out that reliable determinations of exceptionally low Coll-Fe concentrations within the dissolved phase would be impossible from the simple difference between dissolved ($<0.2 \mu\text{m}$ in this study) and soluble values (200 kDa in this study). Therefore, exceptionally low Coll-Fe data in the surface mixed layer in natural condition is nothing but roughly estimate. However, we use the roughly estimated value as one of information for identify that Coll-Fe is minor fraction in dissolved iron phase. In this aspect, our result

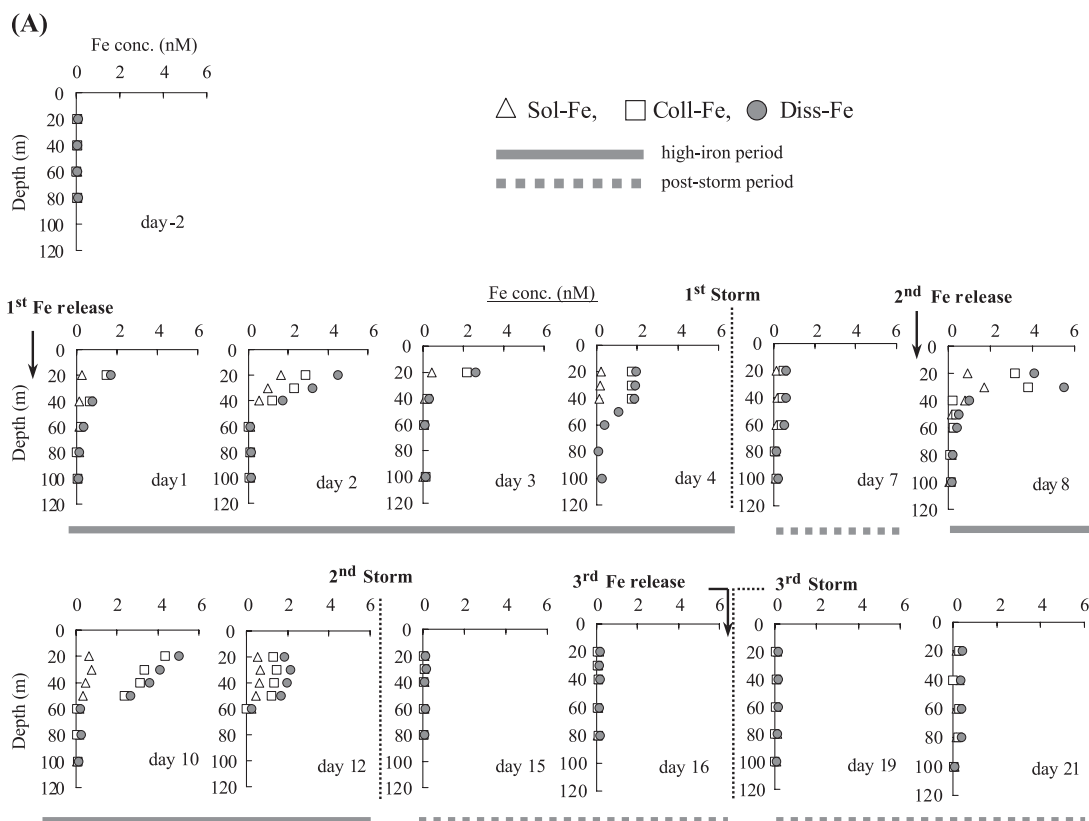


Fig. 3. Vertical profiles of iron concentration in different size fractions at inside of the Fe-enriched patch stations during the experiment, (A) Soluble iron (Sol-Fe), Colloidal iron (Coll-Fe) and Dissolved iron (Diss-Fe), (B) Labile particulate iron (Par-Fe).

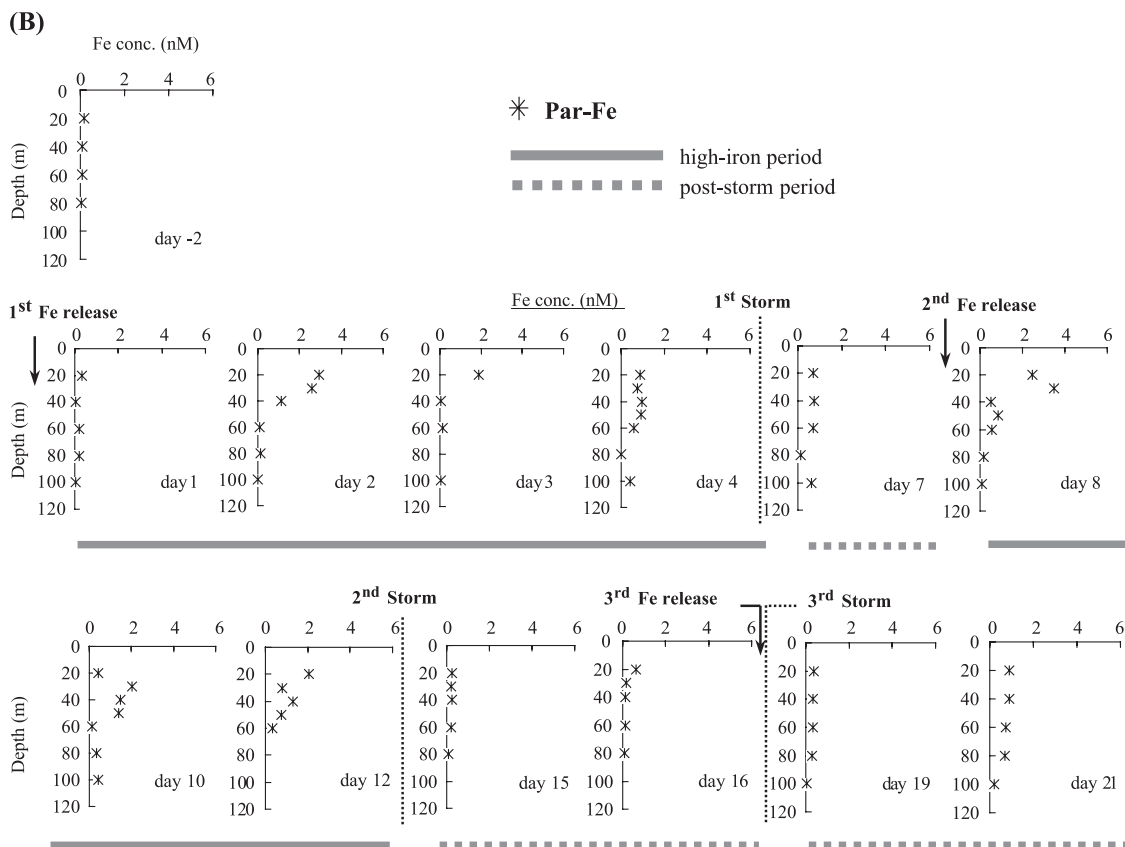


Fig. 3 (continued).

showed that more than half of the “dissolved” iron was in the soluble size fraction in surface mixed layer before iron infusion and in the out patch stations (Table 1). However, Coll-Fe accounted for a significant fraction of “dissolved” pool in the water column below the surface mixed layer (Fig. 2, Table 1). In the surface mixed layer, Coll-Fe comprised about ~35% (roughly estimated value) of Diss-Fe (0.06 ± 0.02 nM ($n=5$)) fraction in the natural condition before iron infusion. This percentage is slightly higher than the average observed in the surface mixed layer in our previous studies in the eastern and western subarctic Pacific (~23%), and that reported in the equatorial Pacific (~15% (Coll-Fe sized: 1 kDa–0.4 μ m); Wells, 2003), but substantially lower than reported for the North Atlantic and North Pacific (80–90%; Wu et al., 2001). As Wells (2003) indicated, these differences may reflect differences in separation methodologies, it also is possible that the Coll-Fe percentage is

influenced by the differing iron supply (aerosol source and redox condition, upwelling, etc.) at each studied site (see Section 4.4).

4.2. Effect of artificial iron addition on iron size-fraction in Southern Ocean seawater

A significant increase of TD-Fe and Diss-Fe concentrations was observed after the first and second iron infusion, and subsequently decreased immediately after storm events. Fig. 6 shows the plot of Sol-Fe, Coll-Fe concentration vs. Diss-Fe concentrations. The data were selected from the surface mixed layer of in patch stations sampling which were conducted in the periods between iron infusions and storm events (defined as the “high-iron period”, Fig. 3). There are significant correlations between the Sol-Fe, Coll-Fe fractions vs. the Diss-Fe fractions indicating that the iron infusions resulted in an

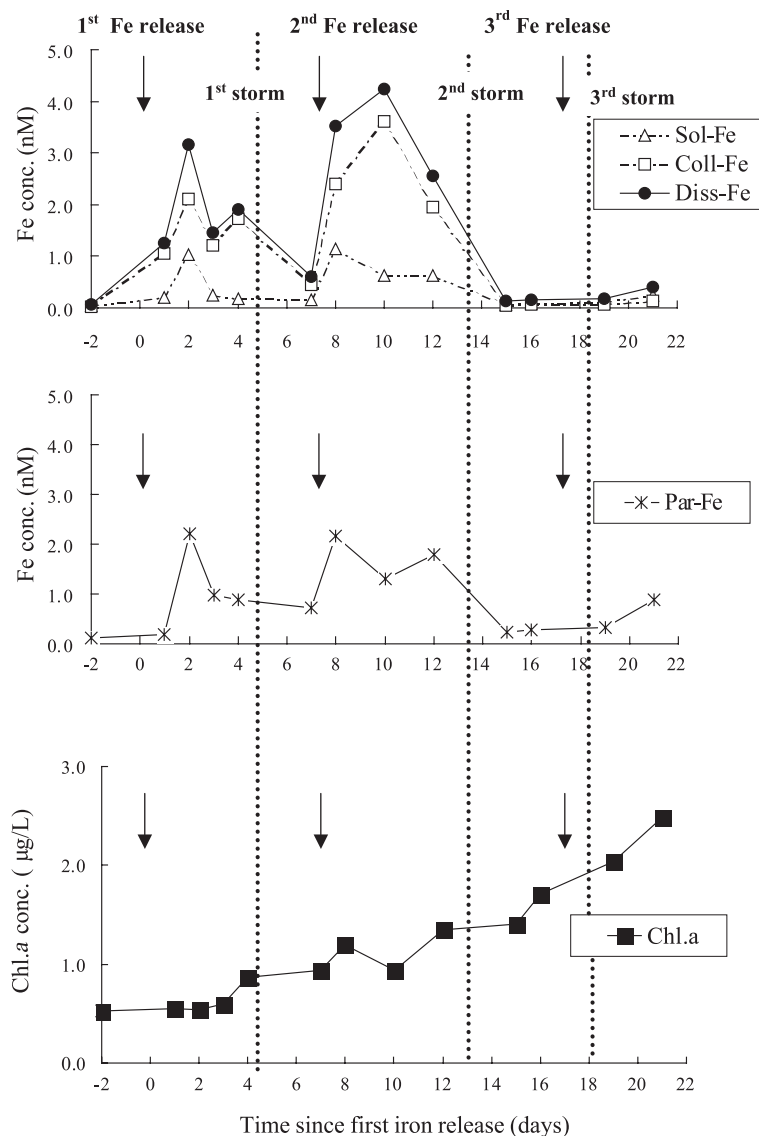


Fig. 4. The changes in size-fractionated iron concentrations, Soluble iron (Sol-Fe), Colloidal iron (Coll-Fe), Dissolved iron (Diss-Fe) and Labile particulate iron (Par-Fe) and chlorophyll *a* (Chl. *a*) concentrations in surface mixed layer inside of the Fe-enriched patch during the experiment.

increasing proportion of Coll-Fe at about 76% of the Diss-Fe (Fig. 6). Moreover, there is also a correlation between the Sol-Fe, Coll-Fe, Par-Fe fractions vs. the TD-Fe (Fig. 6). The slopes of these plots (Fig. 6) indicate that the inorganic iron ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) addition induced the roughly constant proportions of each iron size-fraction (23% in Sol-Fe, 76% in Coll, vs. Diss-Fe) (16% in Sol-Fe, 45% in Coll-Fe, 38% in Par-Fe, vs. TD-Fe) during the high-iron

period, even over a wide concentration range. Average values and standard deviations of the proportions of each iron pool, calculated from same data set, are also shown in Table 1. Our results are consistent with the other two previous in situ iron enrichment experiments (IronEx II; Wells, 2003; SEEDS; Nishioka et al., 2003), also have seen a high proportion of colloidal iron after iron infusion as seen here (79–99%). This result likely reflects the

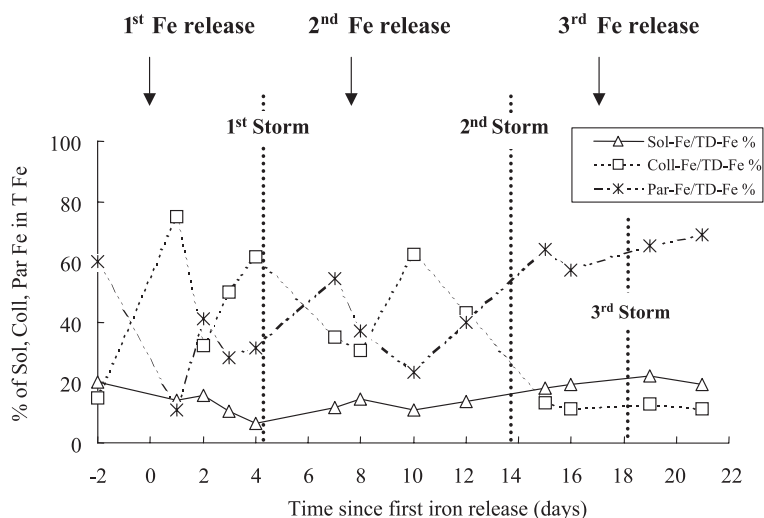


Fig. 5. The changes in the proportion of Soluble iron (Sol-Fe), Colloidal iron (Coll-Fe) and Labile particulate iron (Par-Fe) in Total dissolvable iron (TD-Fe) in surface mixed layer inside of the iron-enriched patch during the experiment.

rapid oxidation of Fe (II) followed by its hydrolyse and precipitation to form colloidal Fe (III) oxyhydroxide (Millero et al., 1987, 1995; Stumm and Morgan, 1996). Although detail in proportion of iron in each size-fraction variable in surface mixed layer (Fig. 5), the plots of every iron data from the high-iron period in the surface mixed layer (Fig. 6) have linearity relationship, even these data has time variations. This result indicates that the proportion of iron in each size fraction was roughly preserved and dramatically transformation of iron among size fraction did not occurred in the high-iron periods.

In other in situ iron enrichment studies, dissolved iron concentrations have decreased rapidly as in IronEx II and gradually in SEEDS study, apparently due to a colloidal iron decrease following aggregation and adsorption to suspended particles (Wells, 2003; Nishioka et al., 2003). In this study, however, Coll-Fe concentrations remained relatively high until the storm events. Immediately following iron infusion, we also observed higher iron concentrations in Sol-Fe fraction than other two experiments (Wells, 2003; Nishioka et al., 2003). This higher Sol-Fe could be due to the different definition of soluble Fe (1 kDa vs. 200 kDa; only for IronEx II) but it might also be related to the lower temperature or concentrations of iron-complexing ligands (high soluble ligands concentrations were observed in this

experiment; see Boye et al., 2004). The stability of added iron here also may depend on physical (e.g. wind mixing, temp.) and chemical conditions (e.g. ligands conc.), however, the reason for this stability is still unclear.

4.3. Changes in proportions of iron size-fractions during EisenEx study

Strong storm events caused Diss-Fe concentrations to decrease in the patch. The third storm dispersed the third iron infusion before it could be sampled. After the first and second storm events and before next iron infusion, and after third storm event (defined to “post-storm period”, Fig. 3), the proportions of Sol-Fe, Coll-Fe, Par-Fe in TD-Fe were $20.6 \pm 8\%$, $17.4 \pm 9\%$ and $62.0 \pm 9\%$, respectively, similar to that measured outside the patch (Table 1). Compared to the proportions during the high-iron period, the proportion of Coll-Fe in Diss-Fe and TD-Fe was significantly low, while, that of Par-Fe in TD-Fe were high during the post-storm period (Table 1, Fig. 5). Storm events caused the iron enriched patch to spread by mixing (Watson et al., 2001), and the iron concentration in every fraction should be diluted in the same ratio by this patch diffusion (if conservative behavior). However, this simple dilution processes alone did not effect the proportions of each

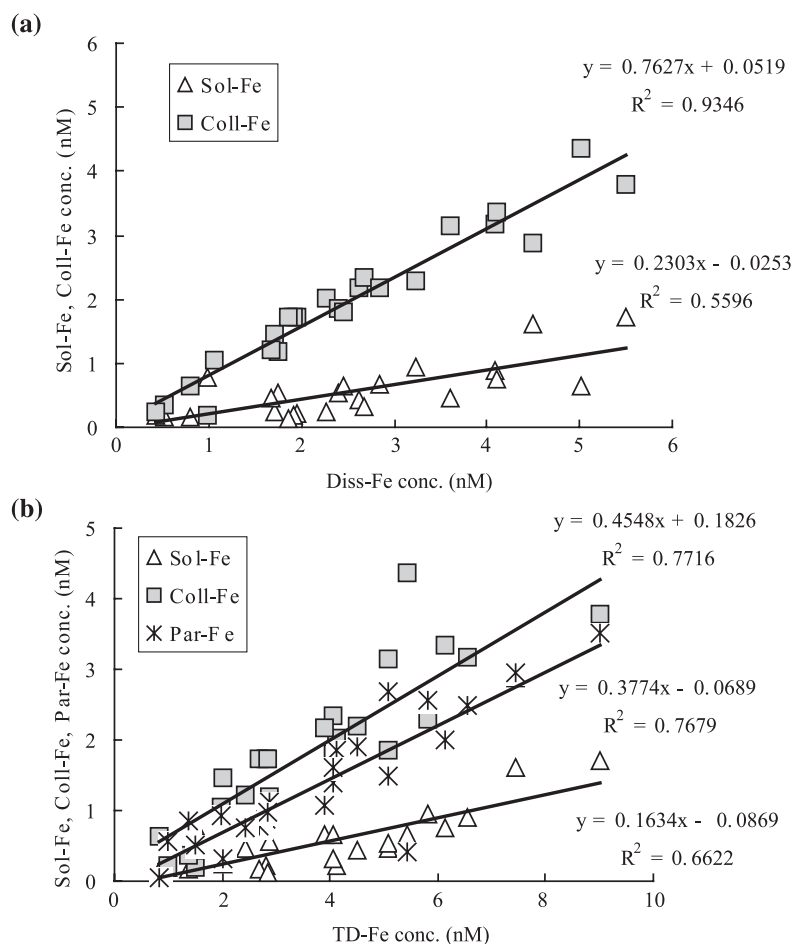


Fig. 6. (a) Soluble (Sol-Fe) and Colloidal (Coll-Fe) iron concentration vs. Dissolved iron (Diss-Fe) concentrations in the patch in “high-iron period” and (b) Soluble (Sol-Fe), Colloidal (Coll-Fe) and Labile particulate iron (Par-Fe) concentration vs. Total dissolvable iron (TD-Fe) concentrations in the patch in “high-iron period”.

iron size-fractionated pool. Instead, Coll-Fe was eliminated from surface mixed layer more easily than the other fractions. Our previous study indicated that the colloidal iron was transformed to particulate iron from chemical/physical aggregation and physical adsorption to suspended particle matter which existed in ambient seawater during phytoplankton bloom (Nishioka et al., 2001a, 2003). The biological response to the iron infusions clearly indicated the increase of biogenic particles in mixed layer in this experiment (Gervais et al., 2002). Mixing of water by storm events might strengthen the selective Coll-Fe removal processes, because mixing may increase the encounter frequency between Coll-Fe and sus-

pended particles, such as phytoplankton cells. Probably, this process occurred simultaneously with dilution process which caused by iron patch horizontal diffusion (the patch spread more than seven times from initial). Measurement of iron-binding organic ligands (Boye et al., 2004) during this experiment showed that organic Diss-Fe and inorganic Diss-Fe would have occurred mainly in the colloidal fraction after iron infusion. They also found that after storm event, colloidal ligands concentrations dropped faster than soluble ligands within the mixed layer, and thus soluble ligands once more dominated the dissolved ligands pool. Moreover, a high proportion (more than 95%) of Diss-Fe during

the post-storm period was bound to organic ligands (Boye et al., 2004). Therefore, our data (this study and Boye et al., 2004) probably indicate that both of organic Coll-Fe and inorganic Coll-Fe were unstable form during storm events. The persistent of Par-Fe and Sol-Fe in the surface mixed layer in the post-storm period may have been due to the presence of suspended particles associated with biota and naturally dissolved organic ligands.

Wu et al. (2001) reported substantial portion of colloidal sized iron in surface of oligotrophic North Atlantic and North Pacific Ocean. Detailed investigations of the behavior of the naturally supplied colloidal iron in the Ocean surface layer is one of unclear point and should compare to artificial iron enrichment study.

4.4. Proportions of iron size-fraction in natural condition

The proportions of Sol-Fe, Coll-Fe and Par-Fe during the post-storm period were very similar to that in the mixed layer of out patch stations (Table 1). The proportion of iron in each size-fraction changed with depth, with Par-Fe decreasing conjunction with increases in Sol-Fe and Coll-Fe (Table 1). Our previous study (Nishioka et al., 2001b) reported that the increase of Sol-Fe and Coll-Fe concentrations below the surface mixed layer correlated with nutrient remineralization, and suggested that the Sol-Fe and Coll-Fe increase below the surface mixed layer resulted from remineralization of biogenic sinking organic particles. Even so, proportions of Sol-Fe and Coll-Fe in Diss-Fe in deep water were significantly different from that in surface water after iron ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) addition, probably reflecting the effects of organic iron ligands and organic colloids. The Sol-Fe and Coll-Fe in deep water include iron which was bound to organic ligands in soluble and colloidal fractions, which were created by decomposition of biota and/or dissolved organic matter aggregation (Wu et al., 2001; Wells et al., 2000; Boye et al., in preparation). Thus, it is apparent that the chemical form of iron is different between an iron enrichment in surface water and deepwater upwelling iron supply. It also implies that the characteristics, species and bioavailability, of natural supplied iron may differ with the supply

source, e.g. between wet–dry iron deposition from the atmosphere and iron input from deeper water vertical upwelling.

5. Conclusion

This study presents results from the application of a physical iron speciation technique to study iron dynamics in the in situ meso-scale iron enrichment experiment in the polar frontal zone of Southern Ocean, EisenEx study. Our results indicate that inorganic iron ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) addition induced high proportions (>76%) of Coll-Fe in the dissolved fraction (<0.2 μm) after iron infusion. The result of changes in proportions of each iron size-fraction after storm events indicate that Coll-Fe is more effectively removed from the mixed layer than other fractions, resulting in high proportions of Par-Fe and Sol-Fe in the surface mixed layer. We also suggest that remineralization of sinking particles induce an increases of Sol-Fe and Coll-Fe in deep water in different proportions from that found after artificial iron addition in surface seawater, because of differences in organic matter influence on iron speciation in deep water. These results suggested that physical speciation of iron study in meso-scale iron enrichment experiment is a useful approach for understanding iron biogeochemical cycles in the ocean and our data suggest that iron removal through colloidal aggregation should be considered in the oceanic iron cycle.

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